

Structural aspects of the dehydration of α -Zr(HPO₄)₂·H₂O

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Abstract

Results of a temperature-dependent crystallographic study of the solid state protonic conductor α -Zr(HPO₄)₂·H₂O are presented. Lattice parameters of this monohydrate and of its dehydrated phases, α -Zr(HPO₄)₂ and β -Zr(HPO₄)₂, have been determined in the temperature range from 20 K to 650 K using X-ray and synchrotron powder diffraction. Neutron data of the protonated and of the deuterated monohydrates were refined by the Rietveld method, paying particular attention to the H- and D-sites, respectively. The dehydration process has been studied by comparing temperature-dependent coherent and incoherent neutron scattering intensities with X-ray powder diffraction and DTA/TG measurements. Proton conduction mechanisms are discussed in the light of these results.

Keywords: Protonic conductor; Dehydration; Zr(HPO₄)₂·H₂O

1. Introduction

The monohydrate of zirconium phosphate α -Zr(HPO₄)₂·H₂O, in the following abbreviated as α -ZP·H₂O, has been studied extensively in the past because of its high ion exchange capacity. More recently much interest has been focused on its protonic transport properties; see for instance Alberti and Casciola [1].

The crystal structure of α -ZP·H₂O was determined by Clearfield and Smith [2]. It is monoclinic, with space group $P2_1/c$, and has the cell dimensions $a = 9.076 \pm 0.003$ Å, $b = 5.298 \pm 0.006$ Å, $c = 16.22 \pm 0.02$ Å, and $\beta = 111.5 \pm 0.1^\circ$. The unit cell contains four formula units. The structure is formed by

zirconium phosphate layers; adjacent layers form cavities, in which the water molecules are located. Each layer consists of Zr⁴⁺ ions arranged pseudo-hexagonally in a plane which is lined on each side by sheets constructed of HPO₄²⁻ tetrahedra. The three oxygens at the basis of each tetrahedron are bonded to three Zr⁴⁺ ions, whereas the fourth carrying an acidic proton is directed towards a neighbouring layer. Thus each zirconium ion is surrounded by a slightly distorted octahedron of phosphate oxygen atoms belonging to six different HPO₄²⁻ tetrahedra. The water molecule is held in the cavity by three intralayer H-bonds (inferred from the O–O distances) involving two phosphate acidic protons and one water proton. The other hydrogen atom of the water molecule forms no hydrogen bond. It is important to note that there are no interlayer H-bonds, so that the layers are held together by van der Waals forces only. This is one of the hydrogen-bonding

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schemes originally proposed by Clearfield and Smith [2] and later confirmed by Albertsson et al. [3] who determined the H-atom positions at room temperature using neutron powder diffraction.

Upon increasing the temperature α -ZP·H₂O exhibits a dehydration reaction. The structure starts to lose H₂O near 100°C, whereby α -Zr(HPO₄)₂ (abbreviated: α -ZP) is formed. Chernorukov et al. [4,5] observed the completion of this dehydration process only near 140°C. At temperatures above 210°C they found a polymorphic transformation to the modification β -ZP, accompanied by endothermic effects. The corresponding heat capacity anomaly has its maximum at 223°C. Both transformations show coexistence of the different phases in relatively large temperature regions. There is also a temperature hysteresis in the case of the α - β transition.

Further heating leads to the loss of a second water molecule per formula unit, for instance observed by Clearfield and Pack [6] in the neighbourhood of 600°C, thus giving the hydrogen-depleted compound Zr-pyrophosphate, ZrP₂O₇. It should be noted that the transformations involving dehydration processes are strongly dependent on external parameters such as heating rate, pressure, and in particular on the water vapour pressure. Such effects have been studied by Krogh Andersen et al. [7].

In the present work we aim at the elucidation of the mechanisms of proton conduction in α -ZP·H₂O and its above-mentioned dehydrated phases by studying the temperature dependent evolution of their structures in general and of the hydrogen atom positions in particular. For this purpose we have reexamined the structure of α -ZP·H₂O and studied that of its deuterated version, α -Zr(DPO₄)₂·D₂O, (abbreviated: α -ZP·D₂O), by powder neutron diffraction. The results are discussed in Section 2. In Section 3 we report on a temperature dependent study of the lattice constants and of the dehydration process as monitored by the measurement of the weight loss, the integrated intensity of incoherent neutron scattering by the hydrogen atoms and the variation of the layer distance. Section 4 deals with some preliminary structure results concerning the β -phase of ZP. Finally in Section 5 we discuss aspects of possible relations between the structure and proton conductivity in this substance.

2. Structure of the monohydrate

The neutron powder diffraction experiments were performed on the diffractometer E6 (protonated compound) and on the flat-cone diffractometer E2 (deuterated compound), respectively, at the 10 MW research reactor BERII in Berlin. Both diffractometers are located on thermal neutron beam holes. The samples were enclosed in cylindrical vanadium tubes with 50 mm height and a diameter of 8 mm.

E6 is equipped with a BF₃ multicounter (resolution 0.1°) covering 20° in 2 θ . Complete spectra in the 2 θ range from 15° to 115° were obtained by moving the detector. A vertically and horizontally focusing graphite monochromator with neutron wavelength $\lambda = 2.4 \text{ \AA}$ and a graphite filter to eliminate higher order reflections were used. E2 is equipped with a BF₃ multicounter covering 80° in 2 θ and was used in a 0.1° angular-resolution mode. A germanium (311) monochromator with $\lambda = 1.21 \text{ \AA}$ and a 10' collimator in front of the monochromator to yield the best available resolution were employed.

The α -ZP·D₂O diffraction data were refined with the Rietveld method (program: PROFIL, V.4.10, 1991, by J.K. Cockcroft) starting with the heavy atom coordinates and displacement factors (i.e. (x, y, z) and B of the atoms Zr, P, O) of Troup and Clearfield [8]. Isotropic atomic displacement factors were used, calculated from the anisotropic ones of these authors, and the atomic coordinates were transformed from the space group $P2_1/n$ to $P2_1/c$. For the deuterium coordinates and corresponding (isotropic) atomic displacement factors the hydrogen results obtained by Albertsson et al. [3] were used as starting values. After the usual determination of lattice constants, monoclinic angle and instrument parameters the refinement proceeded by successive runs liberating first the coordinates and then the displacement factors in the order D, O, P, Zr. The results are shown in Tables 1 and 2. The heavy atom coordinates and B-values agree very well with those of Troup and Clearfield, which are given in the paper of Albertsson et al. [3] who did not refine the heavy-atom positions of those authors. Significant differences as compared to the initial values are only found in the case of (x, y) for D(4), where Albertsson (see Table 3) gives (for H(4)): $x = 0.286(7)$ and $y = 0.273(12)$. Furthermore, as expected, the isotropic atomic displacement factors of D due to the larger mass

Table 1
Fractional coordinates E2-refinement of α -ZP·D₂O

Atom	x	y	z	B (Å ²)
Zr	0.760(1)	0.250	0.514(1)	1.2(2)
P(1)	-0.005(3)	0.746(6)	0.609(4)	1.05(9)
P(2)	0.466(2)	0.256(7)	0.596(4)	1.05(9)
O(1)	0.104(2)	0.803(4)	0.558(1)	1.321(7)
O(2)	-0.057(2)	0.472(4)	0.589(1)	1.321(7)
O(3)	-0.127(2)	0.961(5)	0.602(1)	1.321(7)
O(4)	0.097(2)	0.749(5)	0.709(1)	1.321(7)
O(5)	0.339(2)	0.447(4)	0.554(1)	1.321(7)
O(6)	0.421(2)	-0.027(4)	0.569(1)	1.321(7)
O(7)	0.620(2)	0.302(4)	0.583(1)	1.321(7)
O(8)	0.509(2)	0.251(5)	0.698(1)	1.321(7)
O(9)	0.256(2)	0.222(4)	0.759(1)	1.321(7)
D(1)	0.156(3)	0.900(5)	0.743(2)	4.85(7)
D(2)	0.433(2)	0.255(5)	0.721(1)	4.85(7)
D(3)	0.187(3)	0.388(5)	0.734(2)	4.85(7)
D(4)	0.304(2)	0.215(5)	0.822(1)	4.85(7)

Table 2
Refinement data for α -ZP·D₂O (E2)

Wavelength= 1.2211 Å
Space group: $P2_1/c$
$a = 9.058(2)$ Å; $b = 5.2848(9)$ Å
$c = 16.249(3)$ Å; $\beta = 111.38(1)^\circ$
$U = 2.6(2)$; $V = -1.6(1)$; $W = 0.42(2)$
$R_{wp} = 9.8\%$
$R_{exp} = 3.8\%$
$R_1 = 6.4\%$

are smaller than those of H (Albertsson gives $B = 6.9(8)$).

A refinement of the protonated compound was carried out using the same procedure. Although a smaller R -value than in the deuterated case was obtained, the result had to be rejected because it would have implied too small atomic displacement factors for the O and H atoms, as well as some unreasonable deviations from the expected P–O distances. In a subsequent refinement the following constraints were used: (1) The B-factors of the 4 H-atoms were set equal to 6.0 and kept fixed; (2) The O–H distances were first fixed at 1 Å and the P–O distances at 1.53 Å; this constraint could however be relaxed in the final refinement run. This procedure led to coordinates very similar to those given in Table 2.

Table 3
Fractional coordinates (Ref. [3])

Atom	x	y	z	B (Å ²)
Zr	0.7606(2)	0.250(2)	0.5144(1)	0.67(2)
P(1)	0.0008(6)	0.752(5)	0.6129(4)	1.13(8)
P(2)	0.4711(6)	0.245(5)	0.6044(4)	0.98(8)
O(1)	0.105(2)	0.806(5)	0.560(1)	1.7(3)
O(2)	-0.066(3)	0.486(6)	0.601(2)	2.6(4)
O(3)	-0.131(2)	0.941(5)	0.589(4)	1.6(4)
O(4)	0.104(2)	0.760(9)	0.716(1)	2.2(3)
O(5)	0.344(3)	0.443(5)	0.562(1)	2.0(4)
O(6)	0.418(2)	-0.014(5)	0.569(1)	1.6(3)
O(7)	0.625(2)	0.314(5)	0.590(1)	1.9(4)
O(8)	0.512(2)	0.243(9)	0.705(1)	2.3(3)
O(9)	0.254(2)	0.235(8)	0.759(1)	3.1(4)
H(1)	0.154(7)	0.908(11)	0.737(5)	6.9(8)
H(2)	0.428(6)	0.275(12)	0.734(4)	6.9(8)
H(3)	0.189(8)	0.375(9)	0.734(6)	6.9(8)
H(4)	0.286(7)	0.273(12)	0.813(3)	6.9(8)

3. Structural aspects of the dehydration

We have used X-ray diffraction for a high-precision temperature dependent study of the lattice parameters of α -ZP·H₂O between 20 K and 410 K. The lattice parameters calculated from the Guinier diffractometer data (squares) and from the synchrotron powder diffraction data taken at B2, HASYLAB (circles) are shown in Fig. 1a–e, where it should be noted that the normalization error evident in the overlap region of the data of different origin, is very small (10^{-3} or less). In the temperature range between 20 K and 350 K the unit cell volume behaves according to

$$V[\text{Å}^3] = 713.7 - 1.38 \times 10^{-3}T + 1.33 \times 10^{-4}T^2.$$

The lattice constant c appears to show an anomaly at about 240 K, which might suggest a (so far unknown) phase transition at this temperature. A closer investigation in this temperature region is under way in order to verify whether it is intrinsic or extrinsic. It is obvious from Fig. 1c and d that beyond about 350 K, i.e. upon approaching the temperature region where dehydration starts, the lattice constant c decreases, whereas the angle β increases. Since, in principle, these two parameters may be correlated, it is interesting to study the temperature behaviour of the inter-layer distance. The measured layer spacing d_{002} is plotted in Fig. 2a for the region 300 K to 460 K. It turns out that in the region where the first water molecule is lost, about

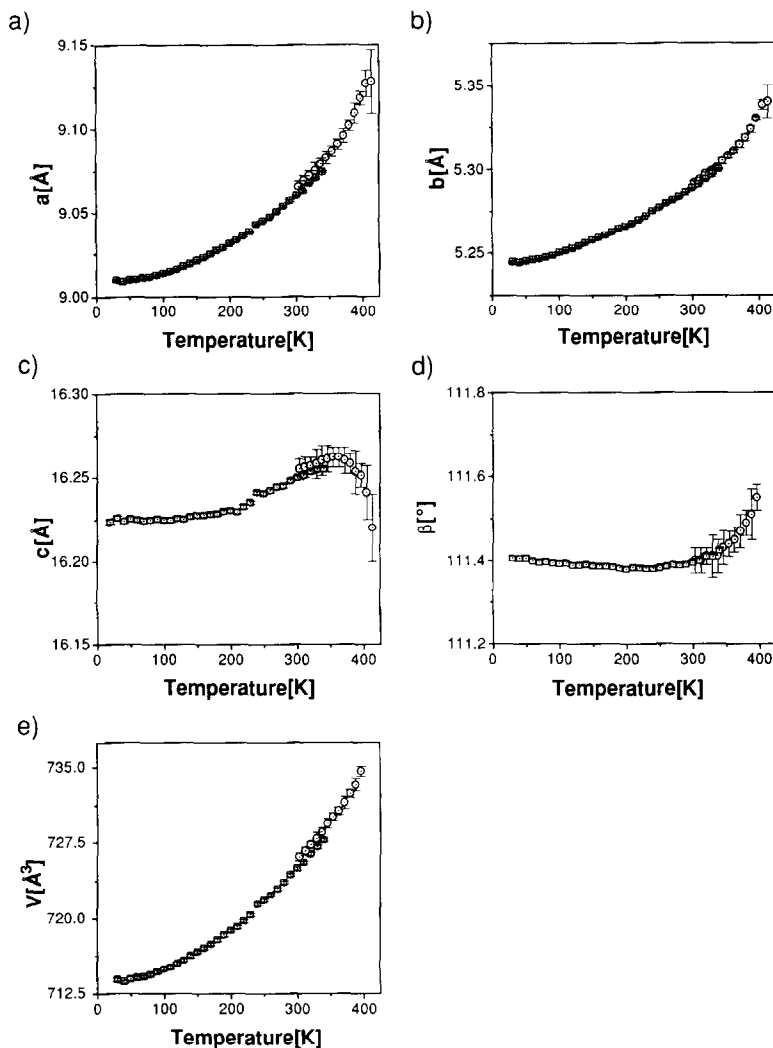


Fig. 1. Temperature dependence of the lattice parameters of α -ZP·H₂O, from Guinier diffraction (squares) and from synchrotron powder diffraction data (circles): (a) to (d) lattice constants and monoclinic angle beta; (e) volume of the unit cell.

390 K to 460 K, d_{002} decreases by about 1%. Furthermore the appearance of the dehydrated α -ZP phase is observed beyond 390 K. Its layer spacing is smaller by about 1.5% than the reference value of α -ZP·H₂O (at 390 K). The composition of the phase mixture present in this temperature region can be estimated from the (002)-peak intensities (Fig. 2b).

A well-known method for monitoring the dehydration process is of course the thermogravimetric (TG) measurement giving directly the weight loss due to the departure of the crystal water. In neutron diffraction experiments the same information can be obtained

somewhat more indirectly, but nevertheless with high precision, by the measurement of the integrated incoherent neutron scattering intensity appearing as a background in between the Bragg peaks. This is demonstrated in Fig. 3. Fig. 3a shows part of a series of 51 powder diffraction diagrams taken at temperatures between 350 K and 850 K. Besides the occurrence of the phase transitions manifested by appearing and disappearing diffraction lines (see Section 1) it is clearly seen already in the powder patterns that the H-scattering background appreciably decreases with increasing temperature. The integral of the incoherent

scattering observed in the region $23^\circ < 2\theta < 27^\circ$ (including a negligibly small background component of different origin) is plotted in Fig. 3b. Two steps are seen corresponding to the loss of the first water molecule per formula unit (here from 350 K to 440 K) and to that of the second water molecule (here from 660 K to 780 K), respectively. The rate of temperature change in this experiment was 0.4 K/min. We also performed TG measurements with different heating rates and have verified that very similar two-step curves are obtained when the rate is the same as in the neutron experiment. It is seen that in such a neutron diffraction experiment it is possible to correlate directly the dehydration reaction and the accompanying structural changes, without the necessity of an additional TG measurement.

A more detailed discussion of the relationship between neutron powder diffraction experiments, with

its various possibilities of data evaluation, and DTA/TG measurements in connection with structural changes across phase transitions will be given in a later publication.

4. α -ZP and β -ZP

So far the structures of α -ZP and β -ZP are unknown. Chernorukov et al. [4] have proposed monoclinic symmetry for α -ZP as well as for β -ZP. According to the powder diffraction data of these authors both phases appear to be isostructural. The difference corresponds to an increase in the lattice constant a and decrease in c , whereas b stays roughly constant, when going from

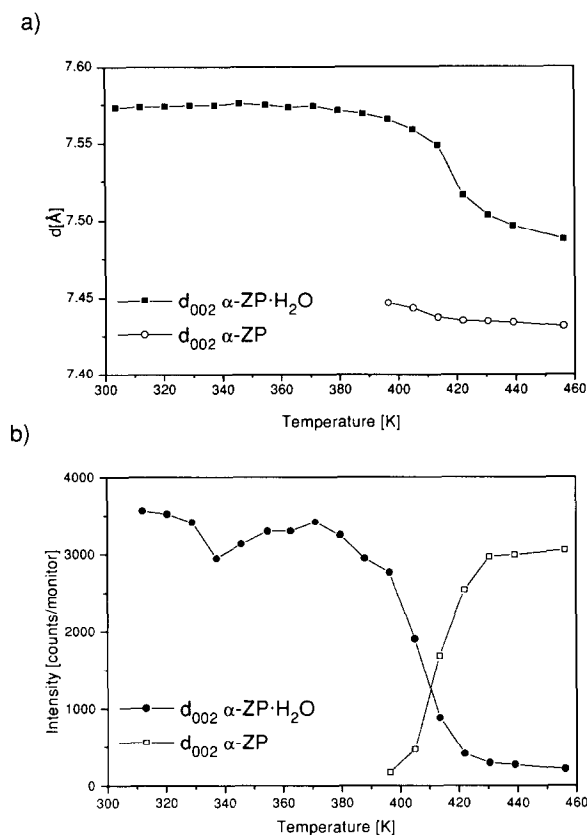


Fig. 2. Dehydration of α -ZP·H₂O, as observed (a) by the temperature dependence of the layer spacing d_{002} and (b) from the behaviour of the 002-peak intensities. Note the appearance of the α -ZP phase above 390 K.

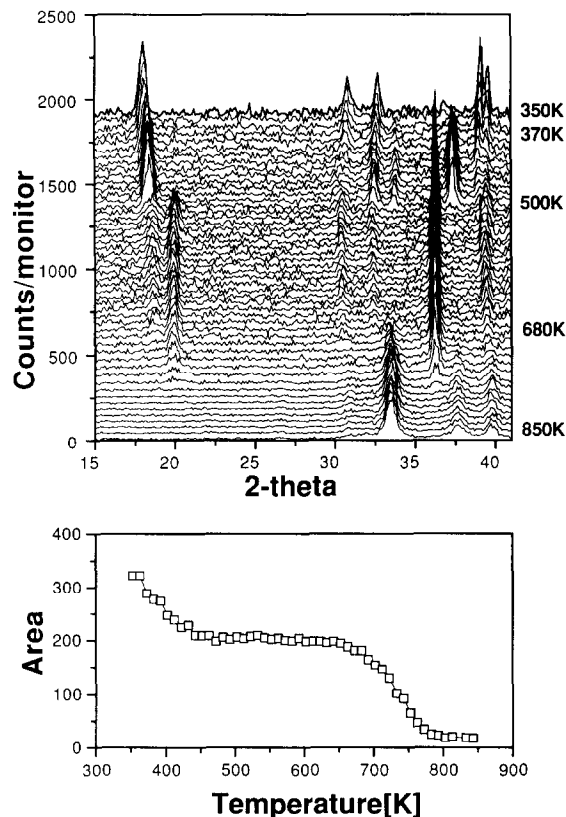


Fig. 3. Dehydration process of α -ZP·H₂O, as monitored by the incoherent neutron scattering intensity observed in between the Bragg peaks: (a) part of a series of 51 powder diffraction diagrams taken between 350 K and 850 K (see text); (b) integrated incoherent scattering observed in the region $23^\circ < 2\theta < 27^\circ$. Note the two intensity steps corresponding to the loss of the first and second water molecule per formula unit, respectively.

the α - to the β -phase. Furthermore the intensities of several reflections change at the transition.

For α -ZP we observe a similar diffraction pattern ($a=9.218(8)$; $b=5.343(2)$; $c=16.08(1)$; $\beta=112.41(9)$; $T=450$ K), but our data clearly show a significantly different variation in the diffraction patterns as one goes through the α - β transition. There are vanishing as well as growing reflections. Part of these effects can be seen qualitatively in the limited range of the diffraction patterns shown in Fig. 3a. The two most intense reflections which start to grow at the transition have also been found by Clearfield and Smith [2]. There are some indications that, depending on the thermal history, α -ZP might not always fully transform into the β -phase, which would then result in the presence of reflections of both phases above the phase transition temperature. This is a possible reason for inconsistency with results published in the literature [2,4]. Taking into account this fact we have made an attempt to index the β -ZP pattern with a hexagonal unit cell with the result: $a=5.3466(1)$ Å and $c=20.505(4)$ Å. A corresponding structure refinement is under way and will be discussed in detail later.

5. Possible relation between structure and proton conduction in ZP

It is known from the experiments by Krogh Andersen et al. [7] that the ac proton conductivity at room temperature of α -ZP·H₂O decreases with increasing particle size, whereas the activation energy (measured in the temperature range from 20°C to 100°C) is independent of the particle size, showing this substance to be a surface conductor. The decrease in conductivity observed at higher temperatures (above about 110°C) [7,9] can be explained as the result of beginning dehydration, whereby the surface water molecules probably are the first to leave the sample.

The influence of the water vapour partial pressure on the dc-proton conductivity σ of α -ZP was studied by Yde-Andersen et al. [10] in the temperature range from 30°C to 107°C. A drastic increase of σ with increasing humidity was observed. At 100% relative humidity (RH) σ -values of 3.2×10^{-4} S cm⁻¹ at 32°C and 1.8×10^{-3} S cm⁻¹ at 107°C, respectively, were found. Qualitatively similar results have been obtained by Casciola and Bianchi [11]. As a consequence of

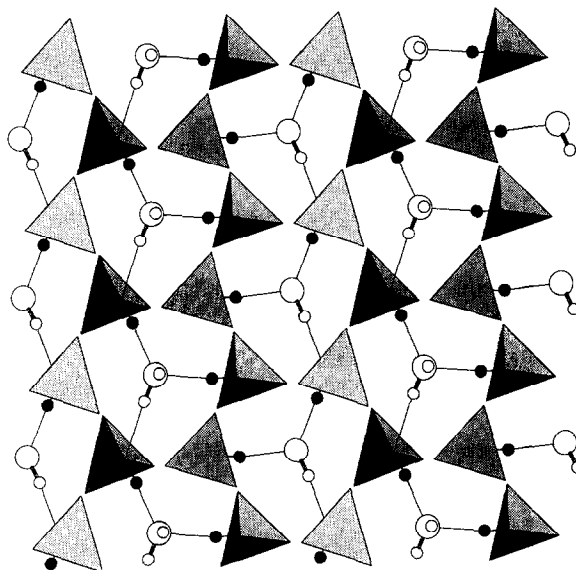


Fig. 4. Projection, perpendicular to the layers, of a (presumably) proton conducting sheet of α -ZP·H₂O containing water molecules (large open circles: O-atoms, small open circles: H-atoms) and acidic protons (full circles). This sheet is lined on each side by a sheet parallel to it, consisting of phosphate tetrahedra. The zirconium ions closest to this triple sheet "sandwich" are arranged in planes parallel to it, above and below, but are not shown in the figure. See text for further explanations.

increasing surface hydration, the dc proton conductivity increases by about two orders of magnitude as the RH goes from 5% to 90% at room temperature. The conclusion regarding the presence of surface as opposed to bulk conductivity is also supported by the fact that the content in bulk crystallisation water is constant in a wide range of RH (from P₄O₁₀ to 100%).

The proton conductivity of anhydrous zirconium phosphate has been studied by Jerus and Clearfield [12] and by Alberti et al. [9,13]. At 200°C the former authors find $\sigma=1.86 \times 10^{-7}$ S cm⁻¹ for α -ZP. At the α - β transition an increase by an order of magnitude is observed and at 300°C they find $\sigma=2.85 \times 10^{-6}$ S cm⁻¹ for β -ZP. Note that in this case we are dealing with bulk proton conductivity and that these conductivity values are much lower than the proton conductivity in α -ZP·H₂O.

After having stated the above experimental facts we will try to relate these to the observations concerning the structure of zirconium phosphate.

Fig. 4 shows for α -ZP·H₂O a projection, perpendicular to the layers, of a (presumably) proton conducting

sheet containing water molecules (large open circles: O-atoms, small open circles: H-atoms) and acidic protons (full circles). This sheet is lined on each side by a sheet parallel to it, consisting of phosphate tetrahedra. The zirconium ions closest to this triple sheet “sandwich” are arranged in planes parallel to it, above and below, but are not shown in the figure. With respect to the atomic distances this arrangement was drawn to scale, using the atomic coordinates of the deuterated compound given in Table 1. The following interesting feature is seen: Each water molecule is connected by H-bonds to phosphate tetrahedra located in the same sheet. Neighbouring water molecules are connected to different sheets. There are no hydrogen sites on straight lines connecting neighbouring “tetrahedral top” oxygens which are the O-atoms approximately located in the conducting plane. Given the large distances between these H-sites observed in the monohydrate, it would not perhaps seem very surprising, if the bulk proton conductivity was very low in α -ZP·H₂O¹. In the case of the anhydrous ZP phases, however, some kind of intermediate sites must also exist to allow for the observed (bulk) proton conductivity in the sheets. But apparently in α -ZP such sites are of such low occupancy that they were not (yet) detected by diffraction, and this in fact explains qualitatively the relatively low value of the bulk proton conductivity.

Let us now turn to the β -phase. This phase has a much higher proton conductivity, which suggests that it might also have a higher crystallographic symmetry, such as trigonal, hexagonal or rhombohedral. Fig. 5 shows a projection similar to that of Fig. 4, but based on a model corresponding to the hexagonal unit cell mentioned above. It is seen that due to the hexagonal symmetry of the suggested proton site arrangement (occupancy 1/3) proton jump distances are obtained, which would make a much higher proton conductivity plausible. Let us note finally that the proposed proton site lattice is similar to that of CsH₃O₂ [14,15]. However, this latter compound has a much higher proton conductivity than β -ZP, probably because the lattice constant of the planar proton site lattice of CsH₃O₂ is smaller by a factor of about 1.3 and the proton jump distances are correspondingly smaller.

¹ While α -ZP·H₂O is known for its high surface proton conductivity, its bulk proton conductivity has not been determined.

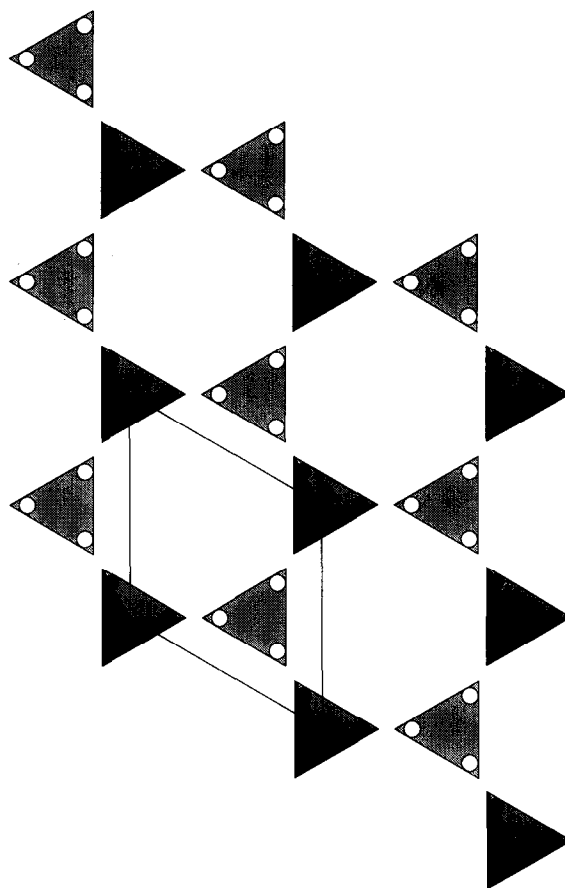


Fig. 5. Projection similar to that of Fig. 4, of a proton conducting sheet for the model proposed for β -ZP, showing a proton site arrangement of hexagonal symmetry.

The model illustrated by Fig. 5 is being examined by a structure refinement currently under way in our laboratory and will be compared to other possible models later.

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